Construction Engineering
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# Sonochemical Degradation Reactions of Nitrobenzene: Oxidation, Reduction, and Dimerization

by Donald M. Cropek
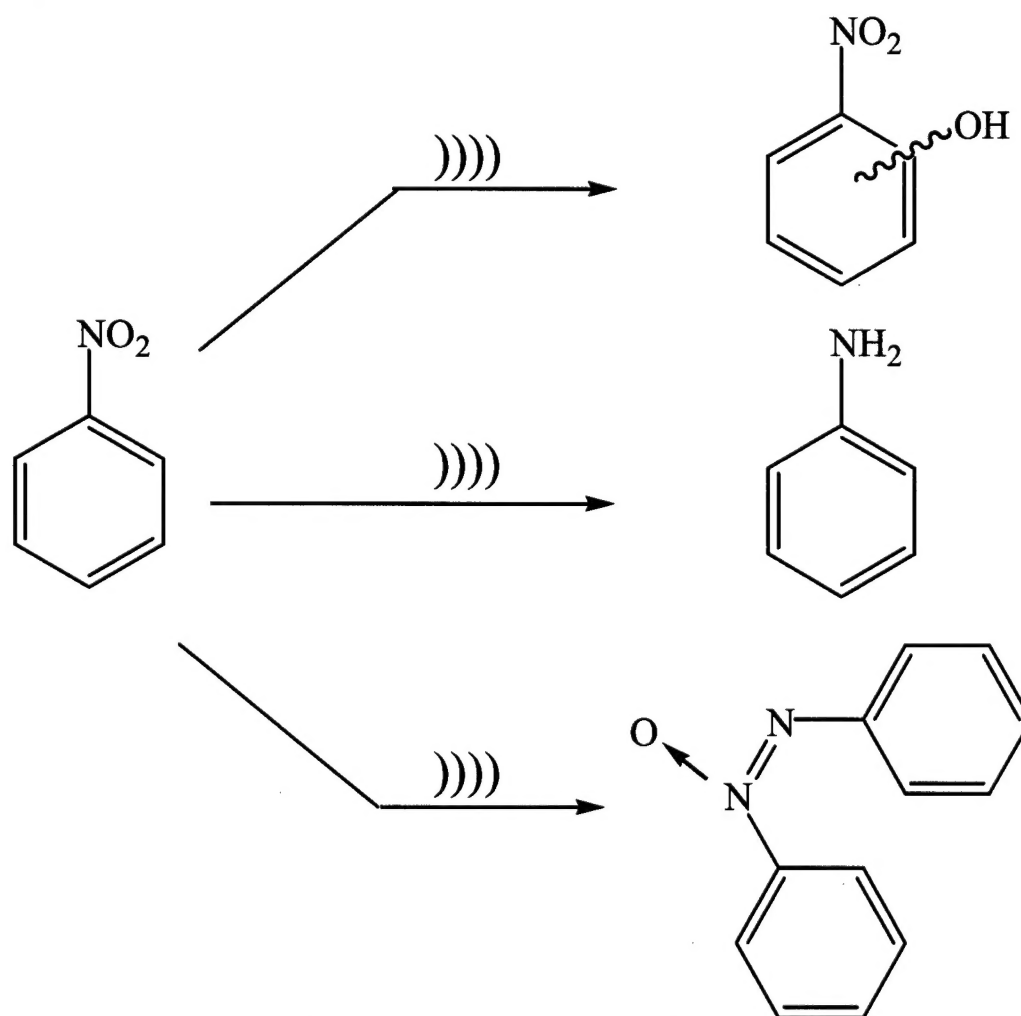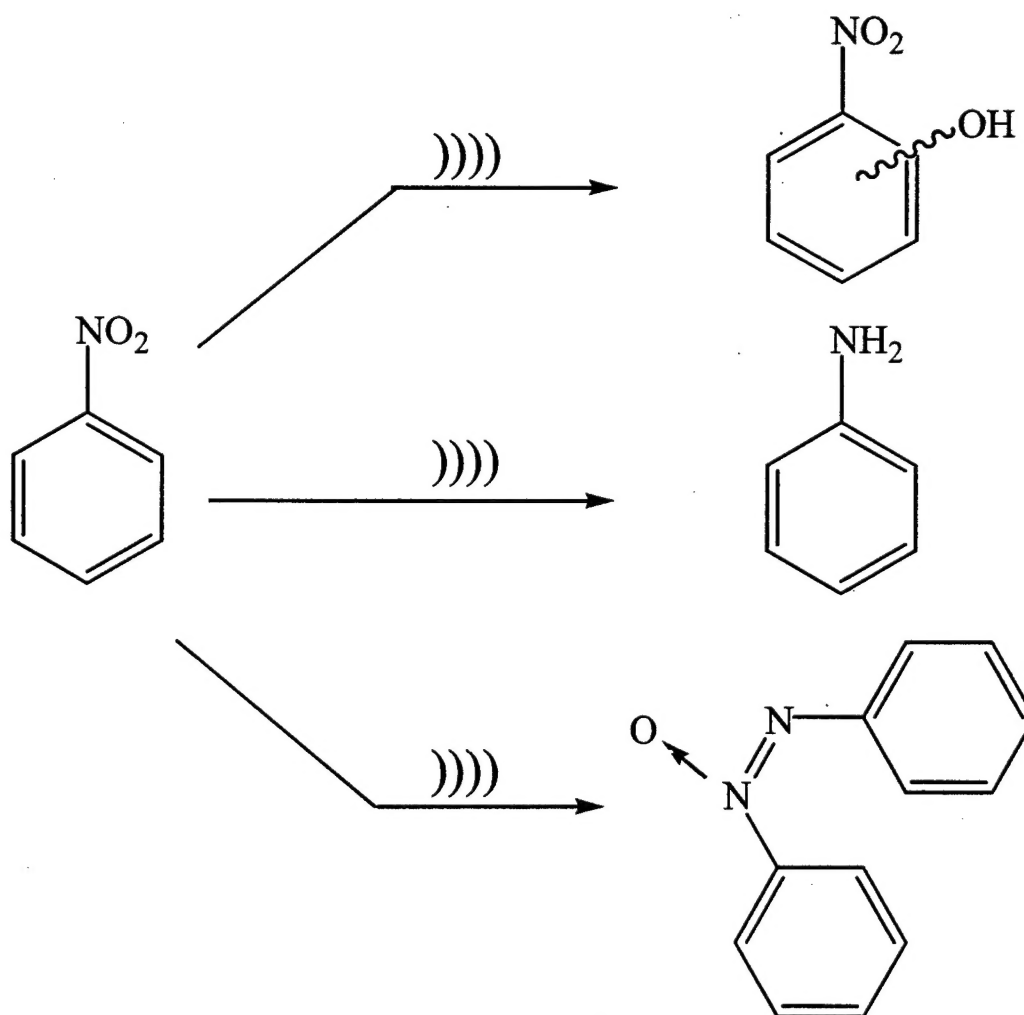
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# Foreword

This study was conducted for Headquarters, U.S. Army Corps of Engineers under 622720D048, "Industrial Operations Pollution Control," U50, "Sonolytic Treatment of Dissolved Energetics." The technical reviewer was Chris Vercautren, Industrial Operations Command, Rock Island, IL.

The work was performed by the Environmental Processes Branch of the Installations Division, Construction Engineering Research Laboratory (CERL). The CERL Principal Investigator was Dr. Donald Cropek. The technical editor was Linda L. Wheatley, Information Technology Laboratory. Dr. Ilker Adiguzel is Chief, CN-E, and Dr. John Bandy is Chief, CN. The associated Technical Director was Gary Schanche. The Acting Director of CERL is William D. Goran.

CERL is an element of the U.S. Army Engineer Research and Development Center (ERDC), U.S. Army Corps of Engineers. The Director of ERDC is Dr. James R. Houston and the Commander is COL James S. Weller.

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# 1  Introduction

## Background

Nitroaromatic compounds are of special interest to the U.S. Army because of their energetic characteristics. They are widely used for military applications, so they are frequently the contaminant of concern in Army wastestreams. The use of ultrasound for the destruction of these hazardous contaminants has become a topic of interest over the last several years.

Sonochemistry is defined as the chemical effects produced by subjecting a chemical reaction to sound waves (Bremner 1990). Ultrasound, with frequencies roughly between 15 kHz and 10 MHz, has a drastic effect on chemical reactions. Ultrasound causes acoustic cavitation, which is the creation, growth, and collapse of bubbles in the solution (Suslick 1989 and Suslick 1990). The collapse produces localized spots of extreme conditions including temperatures as high as 5000 K (Suslick, Cline, and Hammerton 1986) and pressures near 1000 atm (Mason and Lorimer 1988). The extreme conditions created by acoustic cavitation initiate three distinct destruction pathways for organic contaminants: oxidation by hydroxyl radicals, supercritical water oxidation, and pyrolysis. These three mechanisms account for the degradation mechanism for organic species in water. Interest in ultrasound for decontamination arises from its ability to cause these effects relatively inexpensively, with simple equipment and without severe experimental conditions (Shirgaonkar and Pandit 1998).

Several researchers have experimented with sonolytic destruction of organic species in aqueous solutions. These studies include the degradation of chlorinated compounds such as carbon tetrachloride (Francony and Petrier 1996), trichloroethylene (Drijvers et al. 1996), chloroform (Petrier, Reyman, and Luche 1995), pentachlorophenate (Petrier et al. 1992), methylene chloride (Cheung, Bhatnagar, and Jansen 1991), and chlorofluorocarbons (Hirai, Nagata, and Maeda 1996). As further examples, sonolysis of phenol (Petrier et al. 1994; Serpone et al. 1982), arylalkanes (Soudagar and Samant 1995), glyceraldehyde (Fuchs and Heusinger 1995), and pesticides (Kotronarou, Mills, and Hoffman 1992) have also been studied for the purpose of contaminant degradation.

Some work has also been done on the sonolytic destruction of nitroaromatic species in aqueous solutions. The sonochemical reaction of nitrotoluenes in the presence of potassium permanganate oxidizes the $-CH_3$ group to $-COOH$ (Soudagar and Samant 1995). Degradation of p-nitrophenol is primarily by denitration during pyrolysis with radical attack of minor importance to produce $NO_2^-$, $NO_3^-$, benzoquinone, hydroquinone, 4-nitrocatechol, formate, and oxalate (Kotronarou, Mills, and Hoffmann 1991). Sonolytic by-products from trinitrotoluene (TNT) have been studied. The proposed first step is hydroxyl radical attack on the methyl group to form 2,4,6-trinitrobenzoic acid. Other products include trinitrobenzene, hydroxylated TNT derivatives, acetate, formate, glycolate, oxalate, $CO_2$, $NO_3^-$, and $NO_2^-$ (Hoffman, Hua, and Hochemer 1996).

The acoustic cavitation caused by ultrasound produces both hydrogen and hydroxyl radicals upon breakdown of water vapor in the bubble. Curiously, as the above research shows, only the hydroxyl radical seems to play an extensive role in the degradation of nitroaromatics even though the nitro group is already in a high oxidation state. Previous work done in this laboratory also suggests little contribution from the hydrogen radical (Cropek and Kemme 1998). In this report, however, a simple mechanical manipulation of the experimental apparatus is shown to greatly alter the degradation pathway to promote reduction of the nitro group rather than oxidation of the aromatic ring. This report will describe this experimental change and demonstrate the sonochemical reduction of nitrobenzene (NB).

## Objectives

The objectives of this study were to monitor the disappearance of NB and identify the sonolytic by-products that appear. Primary focus was on the discovery of a means to dramatically alter the degradation pathway from oxidation to reduction.

## Scope

This work did not focus on increasing the degradation rate of NB or exhaustively investigating all chemical parameters, but instead noted the manner in which the reduction pathway was enhanced.

## Approach

NB was selected as the initial model compound due to its simplicity and relative safe handling. Aqueous solutions of this compound were sonolytically treated at 20 kHz while changing the physical arrangement of the reaction assembly. Instrumentation for monitoring the progress of degradation included a liquid chromatograph with an ultraviolet (UV)/visible absorbance detector for screening the extent of the reaction and a gas chromatograph/mass spectrometer for identification of by-products.

## Mode of Technology Transfer

It is anticipated that the results of this study will provide information and direction for applied research on the use of sonolysis to treat wastes containing nitroaromatic compounds. Specifically, the results of this work will apply to compliance, pollution prevention, remediation, and demilitarization of aqueous waste streams containing nitrocompounds. Because of its nonspecificity, sonolysis may also provide an additional method to treat other recalcitrant waste streams.

# 2 Experimental Parameters

## Chemicals

Nitrobenzene (NB) (Sigma Chemicals, St. Louis, MO, 99.9%) was used as received. Iron powder (99.99%), iron (II,III) oxide (98%), and nickel powder (99.999%) were obtained from Aldrich Chemical Co., Inc. (Milwaukee, WI). Particle size analysis on the iron powder indicated the following distribution: +200 mesh = 67.1%, +325 mesh = 25.9%, +400 mesh = 5.5%, and -400 mesh = 0.1%. The two-thirds of the iron powder was retained in a 200-mesh sieve, or is greater than 74 $\mu$m in size. The iron (II, III) oxide had an average particle size of 1.85 $\mu$m. The zero-valent nickel powder had the following particle size distribution: +100 mesh = 0.21%, +140 mesh = 1.77%, +200 mesh = 2.14%, and -200 mesh = 95.77%. Almost all the of the nickel powder was smaller than 75 $\mu$m in size.

The acetonitrile used as a mobile phase solvent for liquid chromatography (LC) was HPLC grade (Fisher Scientific, Pittsburgh, PA). Extractions were performed with ether (Aldrich, 99.8% anhydrous) or methylene chloride (Fisher, HPLC-GC/MS grade). All water used for either an LC mobile phase component or during preparation of solution was distilled and deionized with a Milli-Q Plus system (Millipore Systems, Bedford, MA). When preparing the LC mobile phase, both the water and acetonitrile were filtered with a 0.45-$\mu$m pore size nylon filter (Micron Separation, Inc., Westboro, MA).

## Equipment

The progress of sonolysis was monitored using a Waters Associates LC Module Plus 1 liquid chromatograph (Waters Corporation, Milford, MA) consisting of a Model 600 LC pump and a Model 486 UV/Visible absorbance detector. The detection wavelength was 254 nm and the LC column was an ABZ+ column, 25 cm x 4.6 mm, with a 5-$\mu$m diameter particle size (Supelco, Bellefonte, PA). In all cases, the mobile phase was a water-acetonitrile mixture (70:30) with a flow rate of 1.0 mL/minute and an injection volume of 10 $\mu$L.

A Hewlett-Packard (Palo Alto, CA) gas chromatograph/mass spectrometer (GC/MS) system consisting of a 5890 GC, a 5970 mass sensitive detector, and the

G1034C Chem Station operating software was used for the identification of by-products. The column was an HP Ultra 2 capillary column, 25 m x 0.2 mm, with a 0.33 μm film thickness coating of cross-linked 5% phenyl / 95% methyl silicone. The GC method set the injector and detector port temperatures at 200 and 280 °C, respectively. The GC injector was operated in the splitless mode. The GC oven temperature program was held initially at 40 °C for 3 minutes, then was ramped at 20 °C/minute to 280 °C and held for 2 minutes. The total acquisition period was 17 minutes. A 3-minute solvent delay was used. The mass analyzer was set to scan from 30 to 300 amu. The injection volume was 1 μL.

The ultrasonic irradiation of aqueous solutions was performed using a Vibracell Model 600 direct immersion ultrasonic horn (Sonics, Danbury, CT) operated at 20 kHz with a maximum power output of 600 watts/cm$^2$.

## Sonication Experiments

Throughout the experiments, the following parameters remained constant. An aqueous solution of NB was made at 200 ppm (or 1.62 mM nitrobenzene). Approximately 15 mL of this NB aqueous solution was placed into a Suslick cell (Ace Glass, Vineland, NJ). The solution was sparged with ultra high purity argon (AGA Specialty Gas, Danville, IL) for 20 minutes with a 308 stainless steel (SS) needle placed in the solution. The solution was then sonicated with 20 kHz frequency sound waves at an amplitude of 50% in a pulsed manner, 1 second on followed by a 1-second rest period, for 2 hours. This timing equals 1 hour of sonication. The Suslick cell was immersed in a coolant bath to keep the solution cooled to 5 °C during the sonication process.

Six different types of sonication experiments were run using the following additions or deviations from the above procedure.

Experiment Type 1: After sparging, the needle was removed from the solution but remained in the arm of the vessel. The solution therefore was not continuously sparged during sonication but an argon blanket was maintained over the solution.

Experiment Type 2: The needle was left in the solution to continuously sparge the solution with argon during sonication. In addition, the needle physically touched the tip of the probe.

Experiment Type 3: Different types and forms of metals were introduced into the solution before sonication. After sparging, the needle was removed from the

solution so the solution was not continuously sparged but an argon blanket was maintained on top. No metal touched the horn during sonication.

Experiment Type 4: After sparging, the needle was removed from the solution so the solution was not continuously sparged but an argon blanket was maintained on top. Different types of metal wires were configured such that they touched the horn during sonication.

Experiment Type 5: A metal wire was configured to touch the horn during sonication and the solution was continuously sparged during sonication with plastic tubing.

Experiment Type 6: After sparging, the needle was removed from the solution so the solution was not continuously sparged but an argon blanket was maintained on top. The solution was sonicated at 15% amplitude instead of 50% amplitude.

## Analytical Sample Preparation

A 1- to 2-mL sample of a sonicated solution was taken from the reaction vessel and filtered through a Gelman (Ann Arbor, MI) polyvinylidenefluoride (PVDF) filter (0.2-µm pore size) before analysis. Filtration was primarily to remove titanium metal particles produced during sonication via erosion of the titanium tip of the horn. These filtered samples were immediately amenable for analysis by LC. When GC/MS analysis was required, the remaining sample (approximately 14 mL) was extracted with ether or methylene chloride. For complete extraction, the aqueous sample was washed three successive times with the solvent using a 1:3 volume ratio of organic solvent to aqueous solution. These three organic washes were combined and concentrated by a Turbo Vap Concentrator (Zymark Corp., Hopkinton, MA) to a final volume of 1 mL. This concentrated solution was then analyzed by GC/MS via direct injection.

# 3  Results and Discussion

## Nitrobenzene Analysis

Figure 1 shows the structure of NB, the simplest nitroaromatic molecule. Figure 2 shows the chromatogram of the initial aqueous NB solution by LC analysis. The inset of Figure 2 shows the expanded baseline. The NB solution has no discernable contaminants. The retention time of NB is 7.9 minutes. A solution of NB in methylene chloride was analyzed by GC/MS. Figure 3 shows the chromatogram of this NB solution. The inset in Figure 3 shows the expanded baseline. Only the large NB peak is seen at 7.5 minutes. This GC/MS data supports the LC data on the purity of the NB.
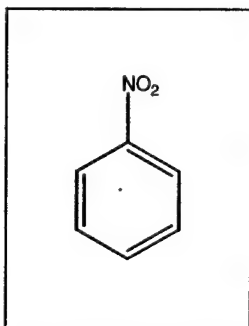


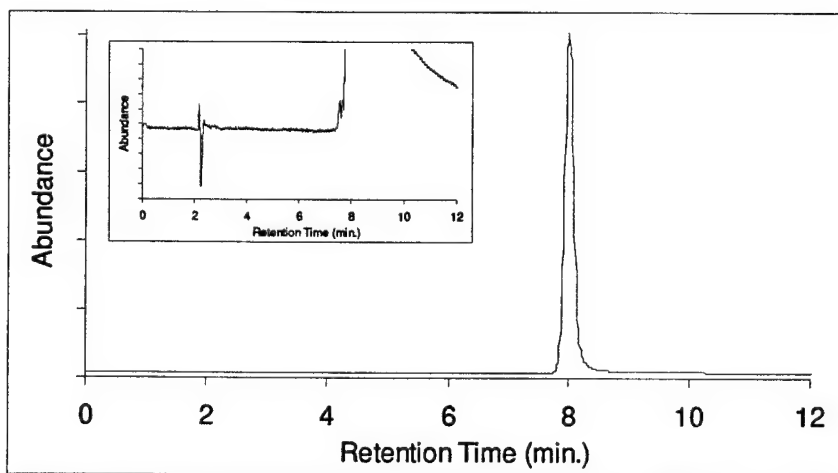**Figure 1.  Structure of NB.**



**Figure 2.  LC trace of the original NB solution before treatment. The inset provides an expanded view of the baseline.**
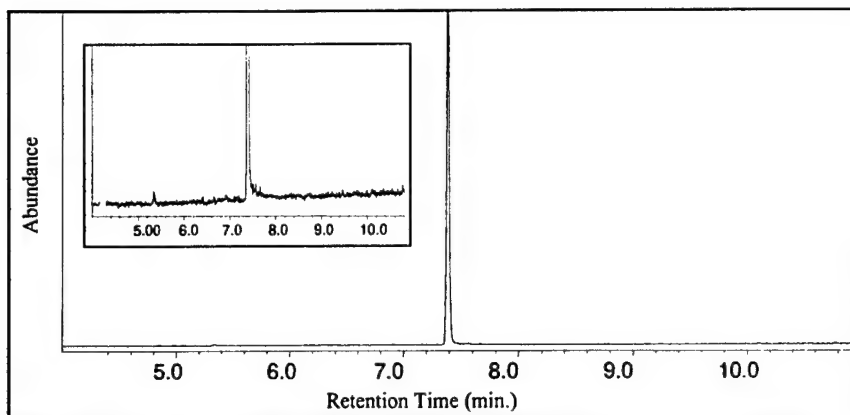
Figure 3. GC/MS trace of the original NB before treatment. The NB peak is observed at 7.5 minutes.

## Experiment Type 1

Sonolysis experiments have usually been performed in this configuration (Cropek and Kemme 1998). Figure 4 shows the LC data of the sonicated solution. This figure is expanded to show the smaller peaks. The large, off-scale peak at 7.9 minutes is NB. Unretained and minimally retained peaks between 2 and 3 minutes dominate the chromatogram. The most important features on this chromatogram are the peaks between 7 minutes and the NB peak. These peaks are due to the three nitrophenol isomers, which are oxidation by-products from sonolysis of NB. The 2-nitrophenol is well resolved at 7.1 minutes, but the 3-nitrophenol and 4-nitrophenol co-elute and are not resolved from the NB peak. Also important for comparison to later data is the lack of any peaks eluting after NB. Figure 5 shows GC/MS analysis of this solution. Table 1 lists the by-products extractable by ether from the sonicated NB solution as identified by numbered peaks in Figure 5. These results agree well with previous data obtained in this laboratory (Cropek and Kemme 1998). Butylated hydroxytoluene (BHT) is a preservative from ether, and phthalates are common laboratory contaminants.

Table 2 lists proposed reactions that take place in this system based on the known reactions occurring during cavitation and the set of by-products from Table 1. The primary reactions are those that occur in the bubble interior during cavitation. These reactions initiate formation of the radical species required for oxidation and reduction. Reaction 1 provides the hydrogen and hydroxyl radicals from the thermal breakdown of water vapor within the bubble. Reaction 3 requires the presence of NB within the bubble for pyrolytic breakdown. It has been proposed that, during sonolysis, this mechanism will decompose NB to form the benzyl radical and nitrite radical with further by-products created from this point (Kotronarou, Mills, and Hoffmann 1991).
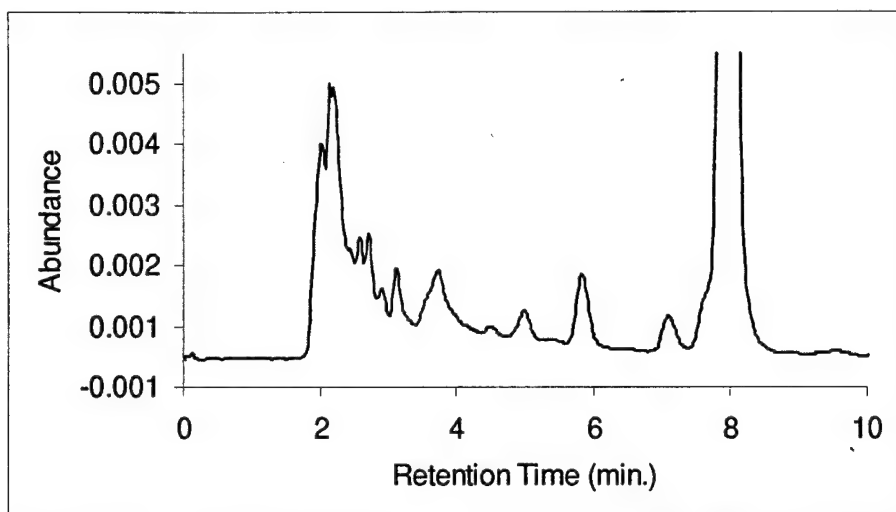
Figure 4. LC trace of the sonicated NB solution from Experiment Type 1.
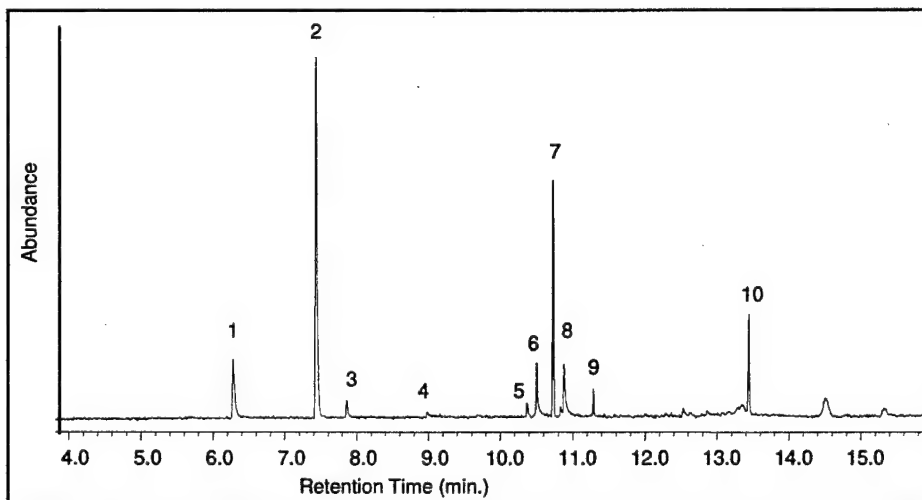


Figure 5. GC/MS trace of the ether extraction from the sonicated NB solution shown in Figure 4.

Table 1. Identification of peaks in Figure 5 based on MS library match.

| Peak Number | By-Product Identification |
|---|---|
| 1 | Phenol |
| 2 | NB |
| 3 | 2-Nitrophenol |
| 4 | Hydroquinone |
| 5 | 1,4-Dinitrobenzene |
| 6 | 3-Nitrophenol |
| 7 | BHT |
| 8 | 4-Nitrophenol |
| 9 | Phthalate (contaminant) |
| 10 | Phthalate (contaminant) |

**Table 2.  List of proposed reactions occurring during sonolysis of NB at 20 kHz, Experiment Type 1.**

Primary Reactions

$$H_2O \longrightarrow \overset{\bullet}{H} + OH^{\bullet} \tag{1}$$

$$O_2 \longrightarrow 2O \tag{2}$$


$$(3)$$

Recombination and Termination Reactions

$$OH^{\bullet} + H^{\bullet} \longrightarrow H_2O \tag{4}$$

$$H^{\bullet} + O_2 \longrightarrow HO_2^{\bullet} \tag{5}$$

$$2H^{\bullet} \longrightarrow H_2 \tag{6}$$

$$2OH^{\bullet} \longrightarrow H_2O_2 \tag{7}$$

$$H_2O_2 \longrightarrow 2OH^{\bullet} \tag{8}$$

Secondary and Termination Reactions


$$(9)$$


$$(10)$$


$$(11)$$


$$(12)$$


$$(13)$$

The second regime includes the recombination and termination reactions. These occur later in time and at a farther distance from the bubble interior. Reactions of this type are not useful for organic degradation. The major termination reaction is Reaction 4, which results in the reformation of water. It has been shown that the superoxide radical from Reaction 5, $HO_2\bullet$, is required for the production of protein microspheres (Grinstaff and Suslick 1991) and may be an active radical species in these degradation reactions. Hydrogen peroxide ($H_2O_2$) is an undesired recombination product in Reaction 7, but may provide a source of hydroxyl radicals after breakdown in Reaction 8.

The final regime contains the secondary and termination reactions. These reactions produce the organic by-products that are detected by LC and GC/MS. Reaction 9 provides the pathway for production of the nitrophenols. Reactions 10 and 11 are two means of producing the nitrobenzyl radical. Further combination with the $NO_2$ radical (Reaction 3) results in the dinitrobenzene molecule (Reaction 12). The only other major pathway requires the hydroxyl radical attack on the benzyl radical from Reaction 3. Reaction 13 combines multiple reactions to produce first phenol, then dihydroxybenzene species. The amount of phenol produced is substantial, and a small amount of hydroquinone is also detected, but no benzoquinone is observed. Based on the by-products, hydroxyl radical attack is a primary degradation method of NB as well as nitrite radical attack, originating from pyrolysis of NB in the hot bubble.

## Experiment Type 2

Figure 6 is an illustration of the sonolysis assembly for this type of experiment. Two major differences are noted in comparing Type 2 to Type 1 experiments. First, the argon bubbles into the solution throughout insonation. Second, the SS needle supplying the argon touches the titanium tip during sonolysis. After 2 hours of pulsed insonation, the needle had cut a groove through the side of the tip and was beginning to cut through the edge of the horn. In addition, the needle had been severed at the contact point with the tip, and the small piece rested at the bottom of the cell.

The LC data from this solution shows behavior quite different from that of the Type 1 data. Figure 7 has a major peak that elutes after the NB peak at 7.9 minutes. The lack of peaks between 7 minutes and the NB peak indicates that formation of nitrophenols is no longer appreciable. Figure 8 is the ether extract of this sonicated solution. The numbered peaks are identified in Table 3. Clearly, the destruction chemistry is following a different pathway. The by-products present in Figure 8 are a result of the increased occurrence of hydrogen

radical attack of the NB. The simple physical manipulation of the stainless steel needle to touch the tip during sonolysis has promoted degradation of NB by reduction instead of oxidation. Reactions 9 – 12 (Table 2) do not occur to a measurable extent and Reaction 6 may be inhibited. Only Reaction 13 remains as phenol is common to both Experiment Types 1 and 2. Table 4 is a list of new secondary and termination reactions that dominate this sonolytic experiment.
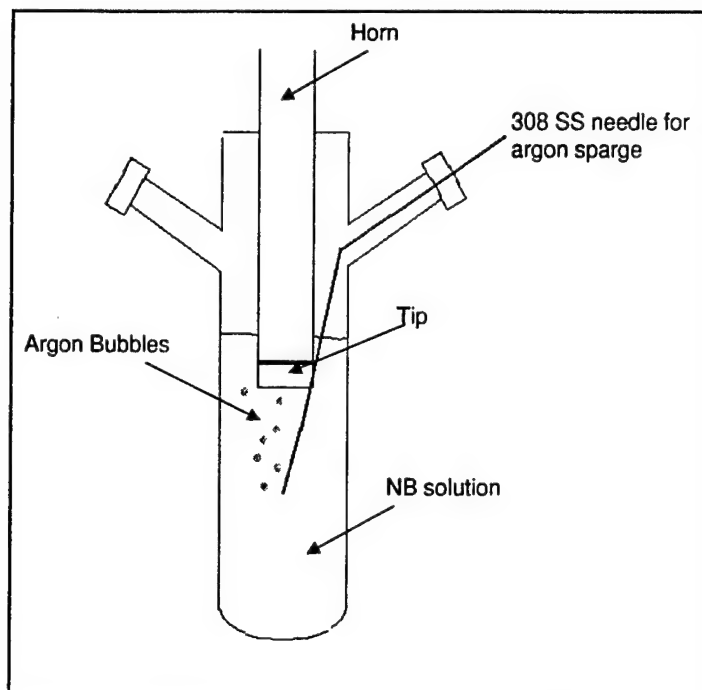


**Figure 6. Diagram of arrangement of Suslick cell, horn tip, and 308 SS needle for argonating Experiment Type 2.**
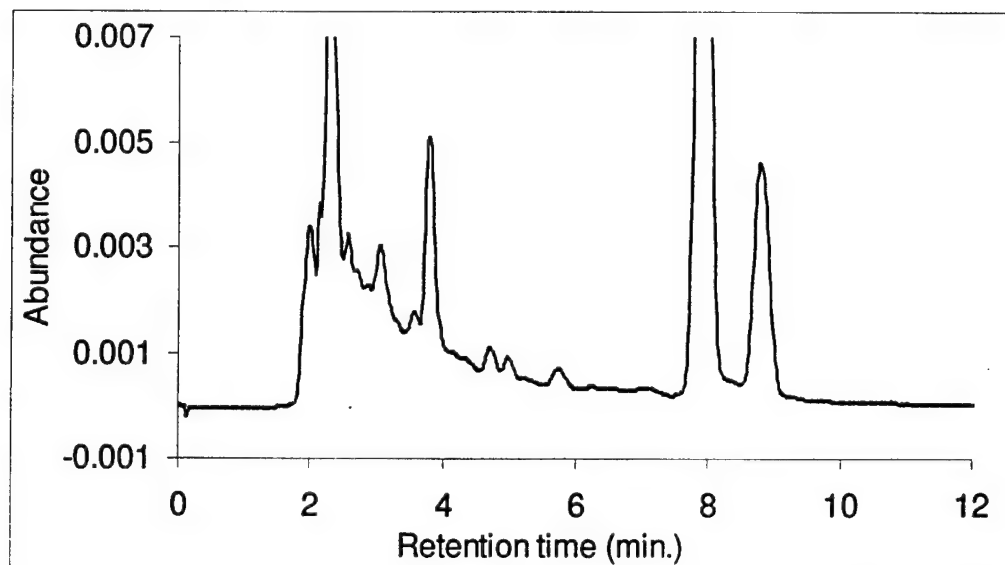


**Figure 7. LC trace of the sonicated NB solution from Experiment Type 2.**
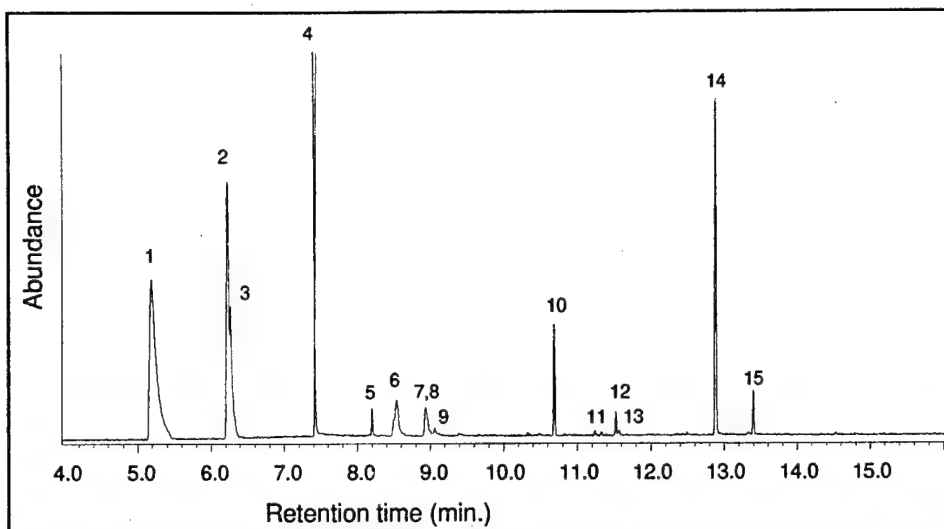
**Figure 8.  GC/MS trace of the ether extraction from the sonicated NB solution shown in Figure 7.**

**Table 3.  Identification of peaks in Figure 8 based on MS library match.**

| Peak Number | By-Product Identification |
|---|---|
| 1 | Nitrosobenzene |
| 2 | Aniline |
| 3 | Phenol |
| 4 | NB |
| 5 | 39,66,95,109 amu |
| 6 | 2-Aminophenol |
| 7 | Resorcinol |
| 8 | 4-Aminophenol |
| 9 | 3-Aminophenol |
| 10 | BHT |
| 11 | Biphenylamine |
| 12 | Hydrazine, 1,1-diphenyl-2-(2,4,6-trinitrophenol) |
| 13 | Azobenzene |
| 14 | Azoxybenzene |
| 15 | Phthalate (contaminant) |

Reaction 14 shows the progression from NB to nitrosobenzene to hydroxylaminobenzene to aniline via successive reductions.  The nitrosobenzene and aniline peaks are prominent by-products in Figure 8.  These two compounds account for the large LC peaks at 37 minutes (aniline) and 8.8 minutes (nitrosobenzene). Peak 5 in Figure 8 is much smaller and did not produce a reasonable peak match from the MS library.  It is proposed, however, that the 109 amu peak in the spectrum is the molecular ion peak and may be the hydroxylaminobenzene species. Aniline can take part in the primary Reaction 15 to create an aminobenzyl radical that can react with the hydroxyl radical to form the aminophenol compounds

(Reaction 16). Azoxybenzene (Reaction 17) is the major by-product formed during sonolysis due to the dimerization of either the nitrosobenzene or the hydroxylaminobenzene compounds. The remaining two reactions show the possible mechanism of formation for biphenylamine (Reaction 18) and azobenzene (Reaction 19). Reaction 19 is merely the combination of two species from the pathway of Reaction 14. These two by-products are present in minute quantities only. The final by-product of note is peak 12 in Figure 8. The MS library search provided a best match of 1,1-diphenyl-2-(2,4,6-trinitrophenyl)hydrazine, a complex combination of three aromatic rings and nitro groups. Although this match is not certain, this type of compound provides evidence of further complicated interactions of intermediate radical species similar to Reaction 19, as well as additional interactions of the nitrite radical from Reaction 3.

**Table 4. List of proposed reactions occurring during sonolysis of NB at 20 kHz, Experiment Type 2.**
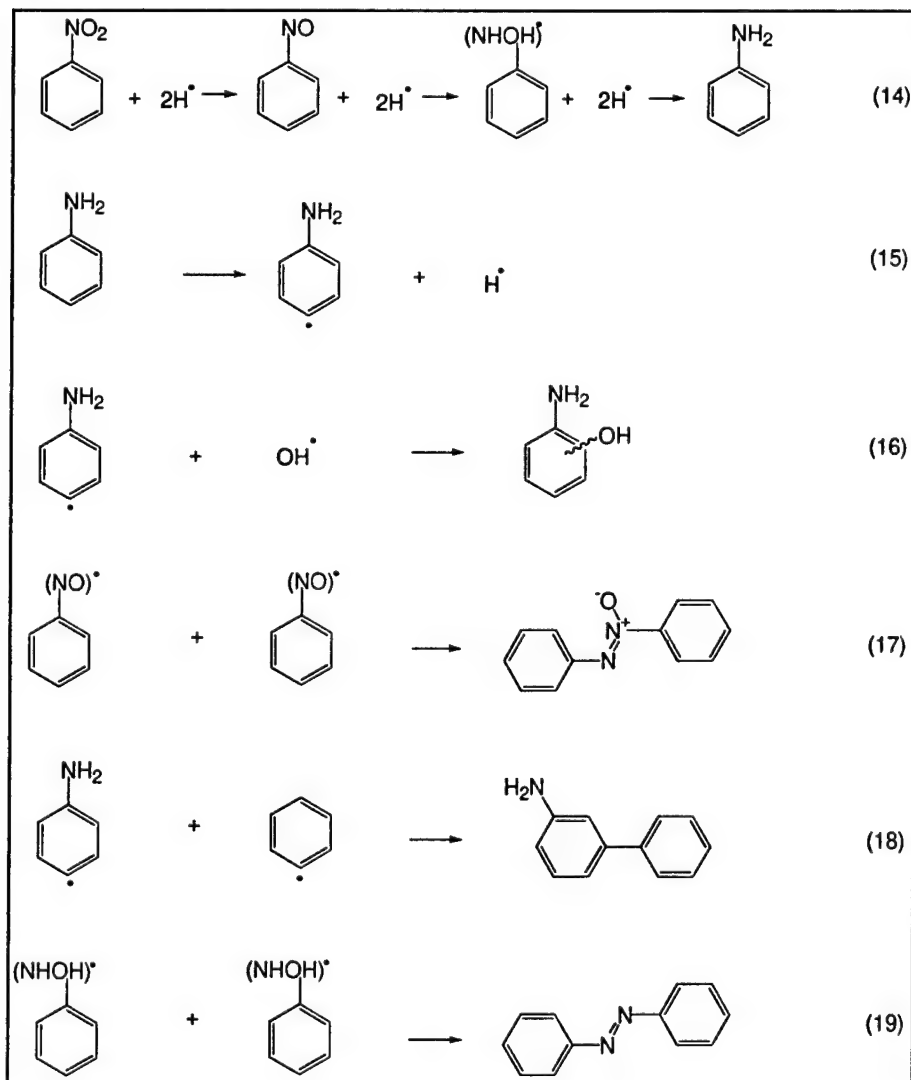
## Experiment Type 3

The remaining experiments were performed to determine why reduction processes dominate in Type 2 experiments. Type 3 experiments were designed to test for catalytic effects of a metal in solution during sonication. A ½-in. piece of the same SS needle from Experiment Type 2 was placed in the NB solution during sonication. Figure 9 shows the results of LC analysis on a sample of this sonicated solution. The large NB peak is observed at 7.9 minutes. No peaks occur after the NB peak and the nitrophenol peaks are clearly visible from 7 minutes to the NB peak. The mere presence of the SS needle is not sufficient to cause reduction.

An experiment with 0.1% (by weight) iron (II,III) oxide powder added to the NB solution prior to sonolysis produced the same LC results as shown in Figure 9. A small ball of fine steel wool was also tried, but the LC results also indicated only oxidation by-products. A final experiment used fine stainless steel 308 wire in the configuration shown in Figure 10. Although a small gap is between the wire and the horn when at rest, the agitation produced during sonication may cause the wire to periodically touch the tip. Again, however, the LC results were the familiar oxidation pattern seen in Figure 9.
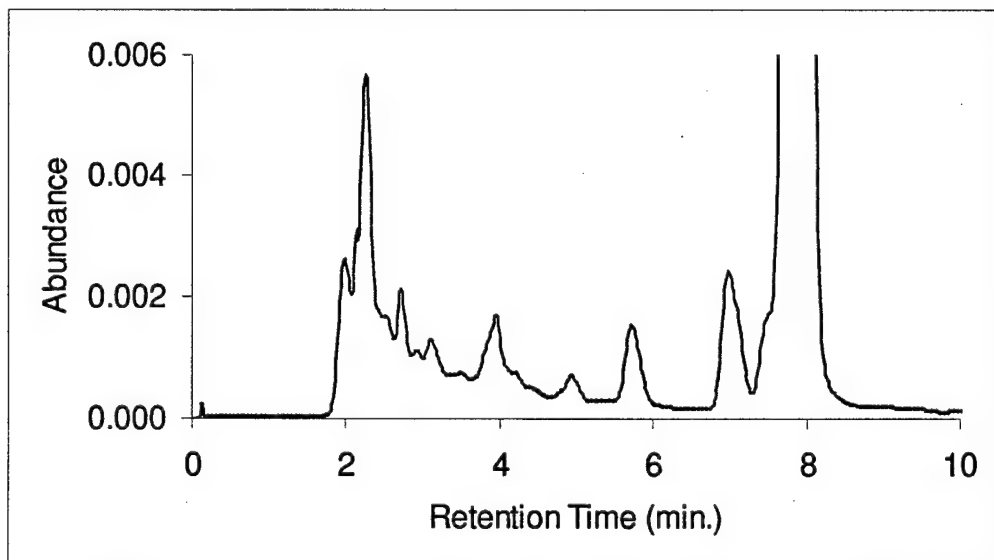


**Figure 9. LC trace of the sonicated NB solution for Experiment Type 3 with a piece of SS needle in the solution.**
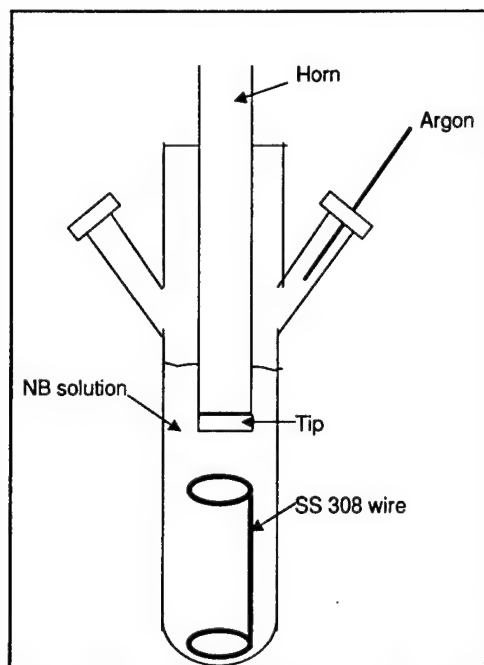
**Figure 10. Diagram of Suslick cell, horn tip, and SS wire for Experiment Type 3.**

Since stainless steel contains primarily iron, nickel, and chromium, two experiments were done using zero-valent iron and zero-valent nickel powder. The LC analysis on the sonicated NB solution containing 0.1% (by weight) zero-valent iron powder is shown in Figure 11. The chromatogram shows no evidence of reduction by-products and the nitrophenol peaks are present. The LC analysis of the sonicated NB solution with 0.1% (by weight) zero-valent nickel powder is similar. When these solutions are extracted with ether, however, many small peaks are observed. Figure 12 is the GC/MS of the ether extraction of the sonolyzed zero-valent iron + NB solution. Table 5 lists the best MS library matches for the numbered peaks in Figure 12. The results for the sonolyzed zero-valent nickel + NB solution are shown in Figure 13 and Table 6. Figures 12 and 13 can be compared to Figure 5 of sonolysis of NB alone. The presence of the metal powders clearly has an effect on the subset of by-products. The most interesting effect is the dimerization of the aromatic species NB and phenol present in the solution. The later eluting peaks are nitrobiphenyl or hydroxybiphenyl compounds. Reactions 3, 10, and 11 from Table 2 are enhanced as well as the production of a phenyl radical that can take part in these reactions. In addition, both metals increase the production of the multiply oxidized by-products such as benzoquinone (nickel), hydroquinone and 1,2-benzenediol (both metals). The iron also catalyzes the production of a compound that appears at 10.8 minutes (peak 9) with a major mass peak at 155 amu. This compound may be nitrohydroquinone, as surmised previously after sonication at 660 kHz (Cropek and Kemme 1998). Based on these results, the presence of these active metals does

not duplicate the remarkable reductive behavior observed in the Type 2 experiments. Iron powder does enhance the slight production of aniline over phenol, but other reductive by-products are absent.
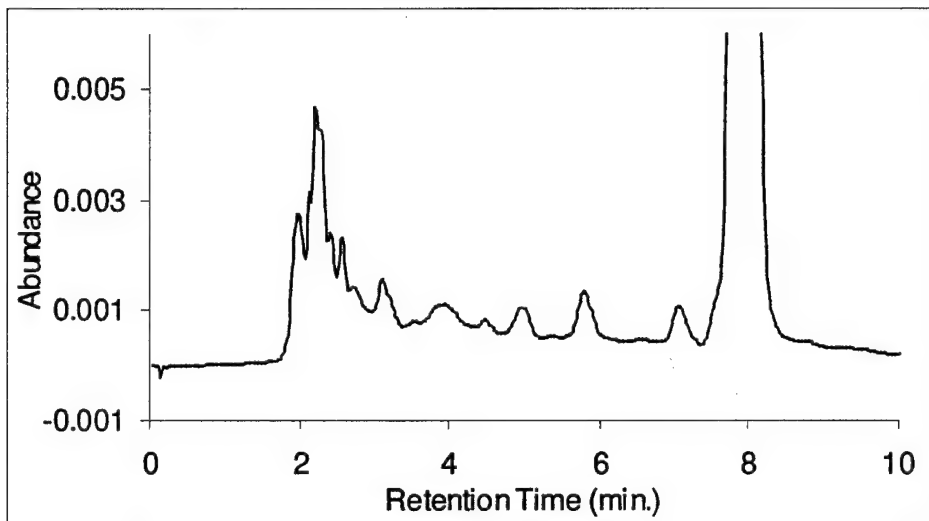


**Figure 11. LC trace of the sonicated NB solution from Experiment Type 3 with added zero-valent iron.**



**Figure 12. GC/MS trace of the ether extraction from the sonicated zero-valent iron with NB solution shown in Figure 11.**

**Table 5. Identification of peaks in Figure 12 based on MS library match.**

| Peak Number | By-Product Identification |
|---|---|
| 1 | Aniline |
| 2 | NB |
| 3 | 1,2-Benzenediol |
| 4 | Hydroquinone |
| 5 | 1,3-Dinitrobenzene |
| 6 | 3-Nitrophenol |
| 7 | Nitroaniline |
| 8 | BHT |
| 9 | 53, 81, 97, 155 amu |
| 10 | 4-Nitrophenol |
| 11 | Phthalate (contaminant) |
| 12 | Background |
| 13 | Diphenylamine |
| 14 | 2-Nitro-1,1-biphenyl |
| 15 | 1,1-Biphenol-3-ol |
| 16 | 3-Nitro-1,1-biphenyl |
| 17 | 1,1-Biphenyl-2,2'-diol |
| 18 | 4-Nitro-1,1'-biphenyl |
| 19 | Phthalate |
| 20 | Dinitrobiphenyl |
| 21 | Phthalate (contaminant) |



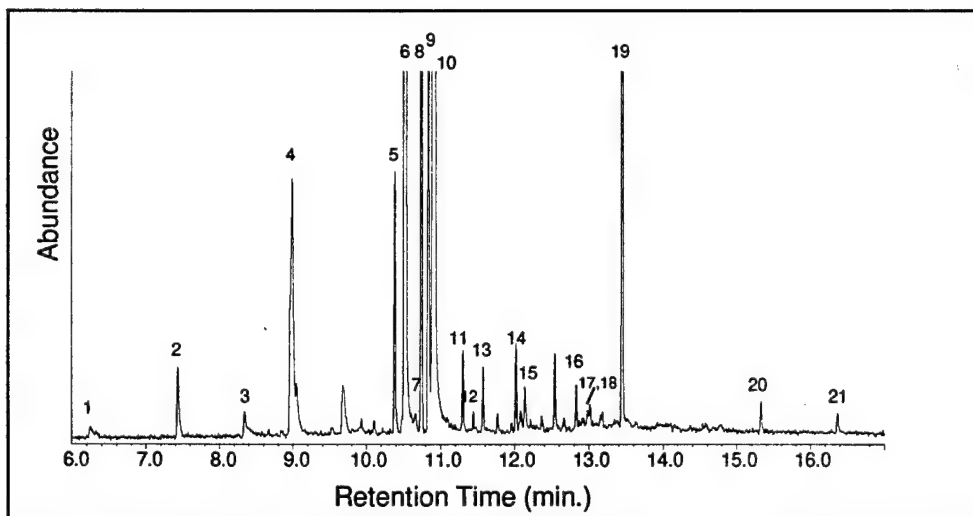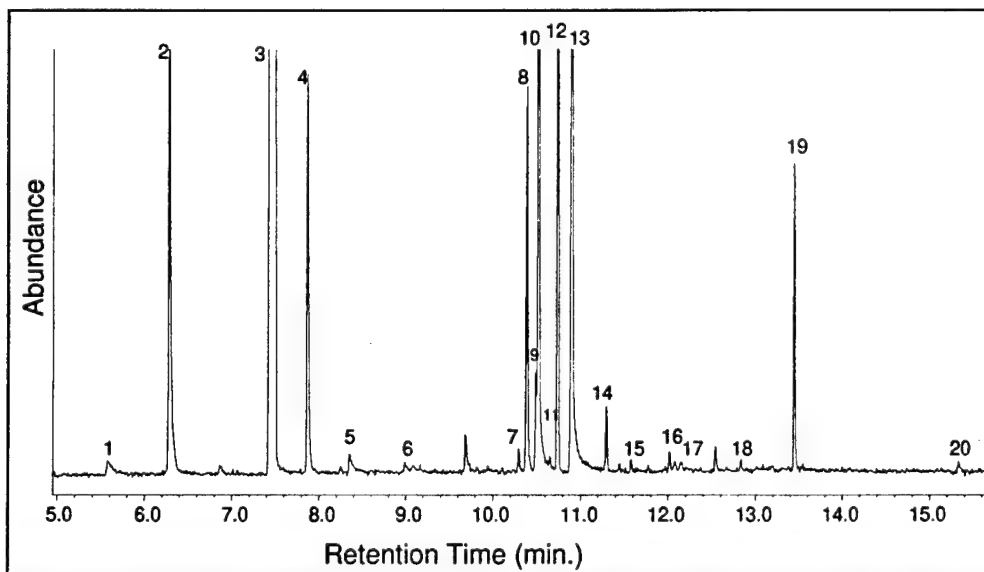**Figure 13. GC/MS trace of the ether extraction from the sonicated zero-valent nickel with NB solution.**

**Table 6. Identification of peaks in Figure 13 based on MS library match.**

| Peak Number | By-Product Identification |
|---|---|
| 1 | Benzoquinone |
| 2 | Phenol |
| 3 | NB |
| 4 | 2-Nitrophenol |
| 5 | 1,2-Benzenediol |
| 6 | Hydroquinone |
| 7 | 1,4-Dinitrobenzene |
| 8 | 1,3-Dinitrobenzene |
| 9 | 1,2-Dinitrobenzene |
| 10 | 3-Nitrophenol |
| 11 | Nitroaniline |
| 12 | BHT |
| 13 | 4-Nitrophenol |
| 14 | Phthalate (contaminant) |
| 15 | Diphenylamine |
| 16 | 2-Nitro-1,1'-biphenyl |
| 17 | 1,1-Biphenol-3-ol |
| 18 | 3-Nitro-1,1-biphenyl |
| 19 | Phthalate (contaminant) |
| 20 | Dinitrobiphenyl |

## Experiment Type 4

Instead of experiments where the metal does not touch the horn or tip, this type of experiment strives for intimate contact between the vibrating horn and a metal wire. Figure 14 shows the general configuration of wire and horn during sonication. In this arrangement, the wire is wound around the horn, loops beneath the titanium tip, but does not necessarily touch the tip. Using thin 308 SS wire, the sonolysis of the NB solution results in the LC shown in Figure 15. Aging of the ABZ+ column has caused a shift in elution times. NB is now observed at 7 minutes. No nitrophenols are observed, but there are also no peaks eluting after the NB peak. Methylene chloride extraction of this solution and subsequent analysis by GC/MS gives the data shown in Figure 16. Only three peaks are observed, nitrosobenzene at 5.3 minutes, aniline at 6.3 minutes, and NB at 7.5 minutes. On the shoulder of the aniline peak, a very small phenol peak is also present. Nevertheless, sonication with the metal wire in contact with the vibrating system appears to alter the degradation pathway to promote reduction over oxidation.
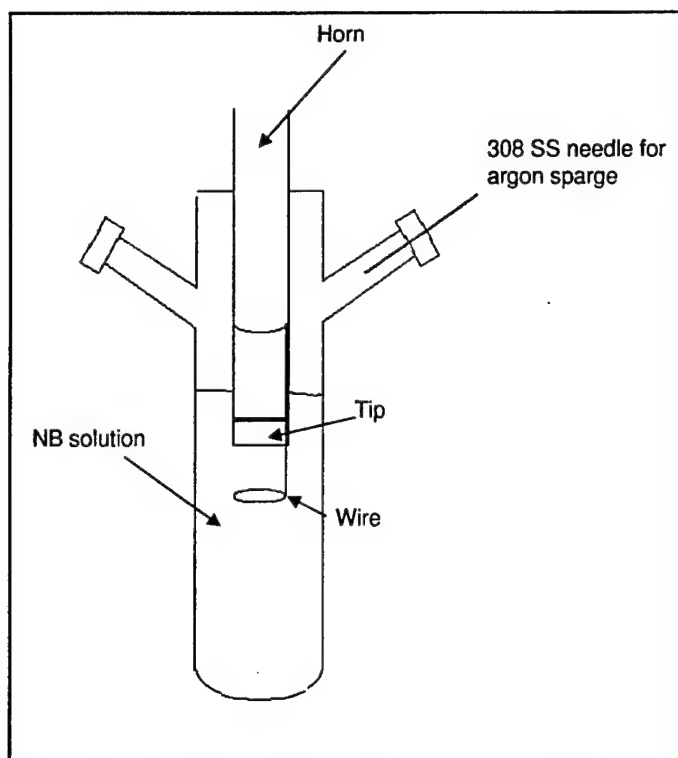
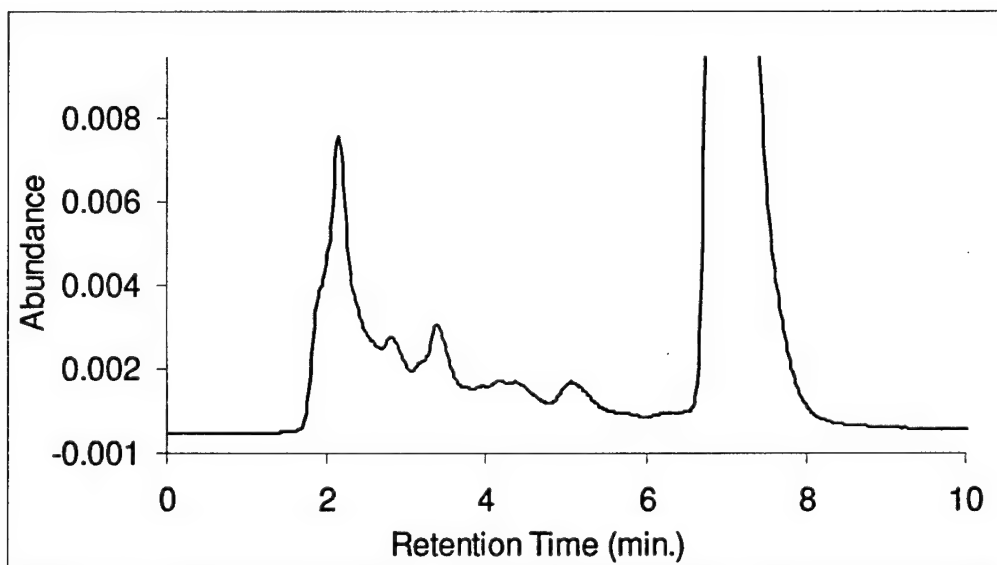**Figure 14. Diagram of Suslick cell, horn tip, and wire for Experiment Type 4.**



**Figure 15. LC trace of the sonicated NB solution with SS wire in contact with the horn in Experiment Type 4.**

**Figure 16. GC/MS trace of the methylene chloride extraction from the sonicated NB solution shown in Figure 15.**

Nickel wire was also used in the configuration of Figure 14. The LC analysis of the sonicated solution had similar characteristics to the stainless steel wire experiment shown in Figure 15 although the aniline peak at 3.4 minutes was more prominent. GC/MS analysis of the methylene chloride extraction is shown in Figure 17. Aniline at 6.3 minutes is the only appreciable by-product observed. Nitrosobenzene can be extracted from the MS data as a very small peak at 5.3 minutes. All other small peaks are septum bleed compounds.
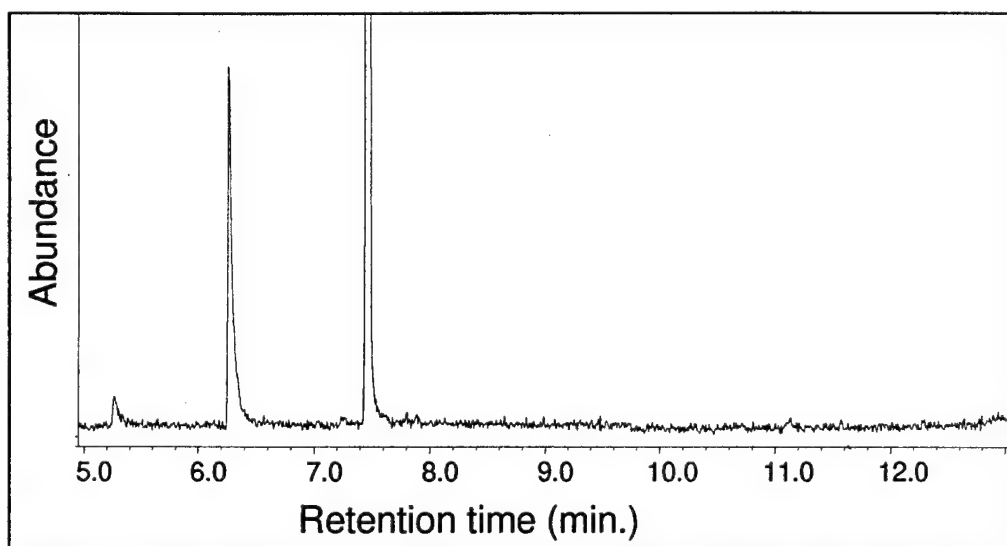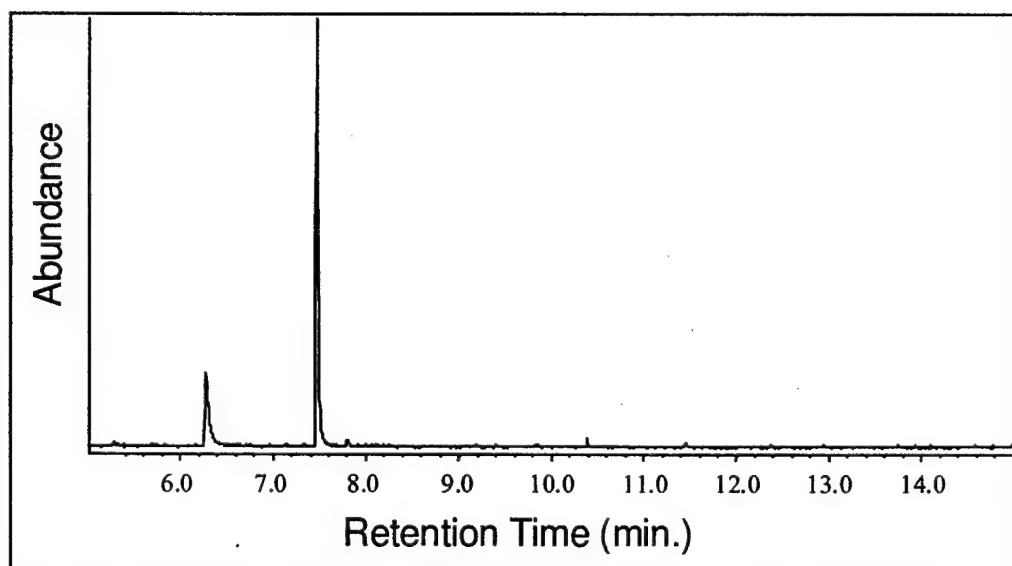


**Figure 17. GC/MS trace of the methylene chloride extraction from the sonicated NB solution using nickel wire wound around the vibrating horn.**

## Experiment Type 5

One experiment was done in this configuration using 308 SS wire. The wire was used in the manner shown in Figure 14. Plastic tubing was used to continuously sparge the solution with argon throughout sonication. The LC analysis of NB solution sonicated with this arrangement is shown in Figure 18. This chromatogram has all the features of only reduction by-products. The aniline peak is large at 3.4 minutes, there are no nitrophenol peaks between 6 and 7 minutes, and a later eluting peak appears as a shoulder on the NB peak that is identified as nitrosobenzene by comparison with a standard. A methylene chloride extraction of this solution was analyzed by GC/MS, and Figure 19 shows this chromatogram. Again, the nitrosobenzene and aniline peaks are the only by-products observed. Comparing the LC results of this experiment (Figure 18) with the LC results from Experiment Type 4 (Figure 15), the NB peak is smaller and the by-product peaks are correspondingly larger in Figure 18. It appears that sparging with argon during sonolysis increases the degradation rate of NB and, therefore, the concentration of reduction by-products.
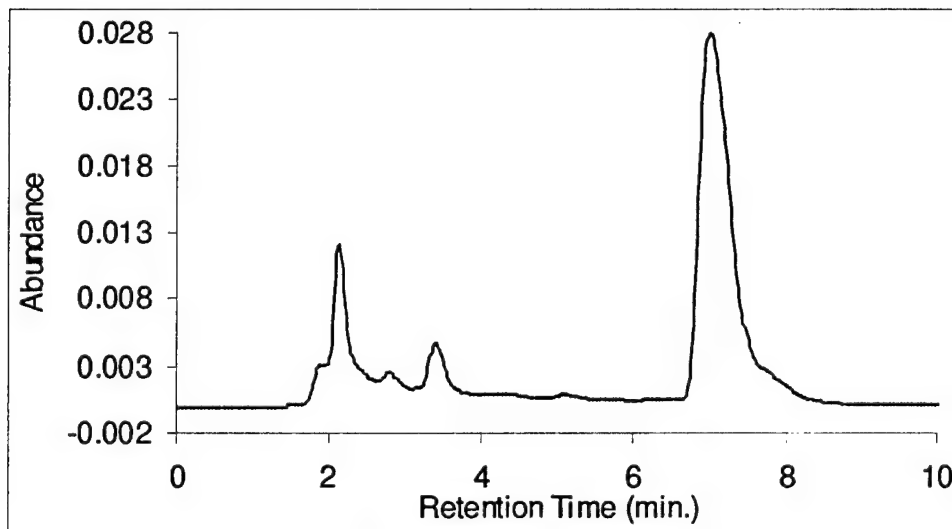


**Figure 18. LC trace of the sonicated NB solution from Experiment Type 5.**
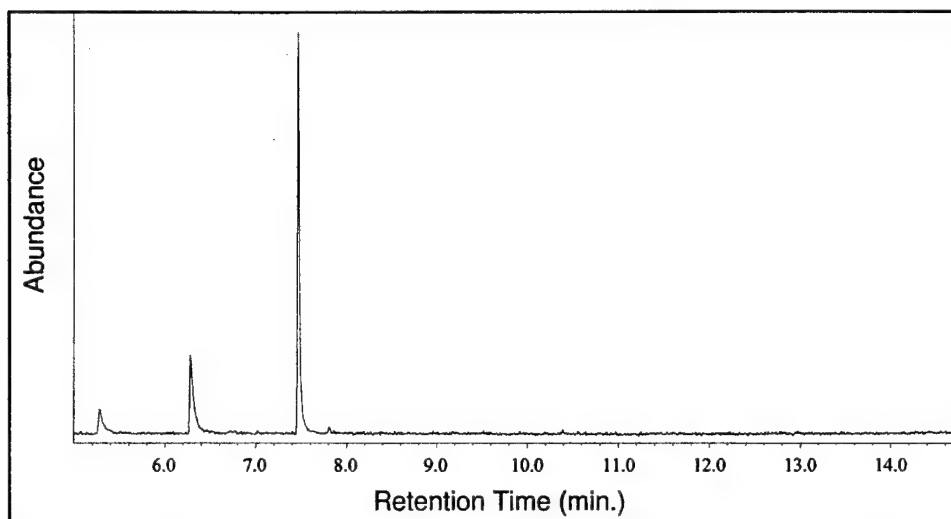
Figure 19. GC/MS trace of the methylene chloride extraction from the sonicated NB solution shown in Figure 18.

## Experiment Type 6

According to Sonics, Inc., touching the tip of the probe will not alter the vibration frequency but will decrease the amplitude. One experiment was performed with no metal touching the tip, but the amplitude was significantly reduced from 50 to 15%. Figure 20 shows the LC analysis of the sonicated solution of NB using 15% amplitude. The extent of NB degradation is lower than in other experiments since the peak height of NB is larger while the production of by-products is less. Small peaks in the nitrophenol region (7 – 8 minutes) can be seen, but no new peaks are observed eluting after NB. The ether extraction of this sonicated solution was analyzed by GC/MS, and Figure 21 shows the results. Few by-products are observed; specifically, nitrosobenzene at 6.5 minutes, aniline at 8.4 minutes, phenol as a broad peak at 9 minutes, and 2-nitrophenol at 11.7 minutes. The ether preservative BHT is seen at 18.6 minutes.
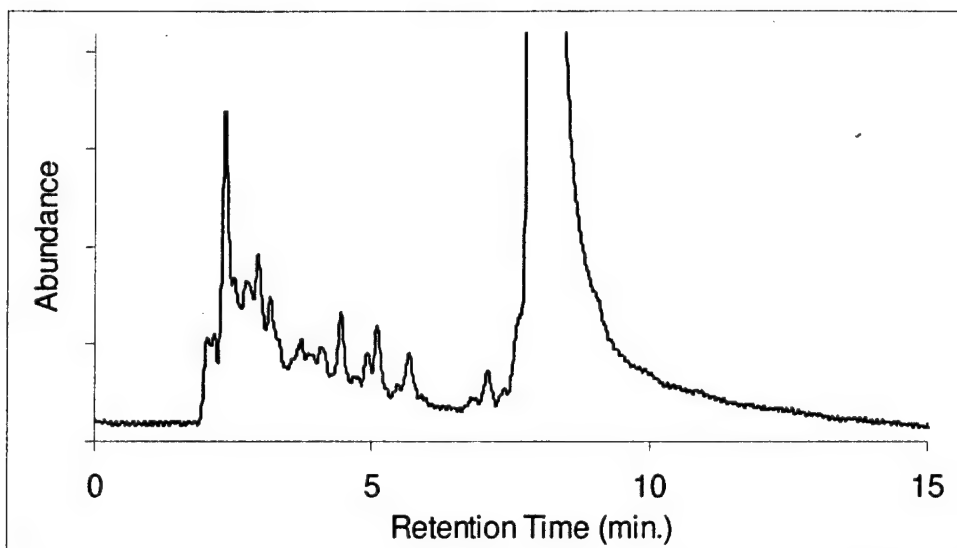
Figure 20. LC trace of sonicated NB solution from Experiment Type 6.
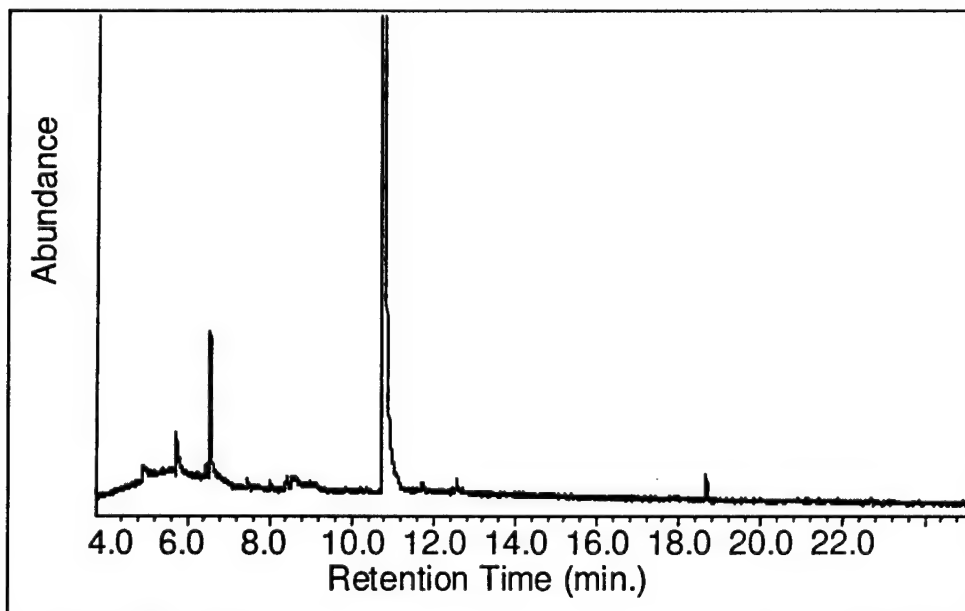


Figure 21. GC/MS trace of ether extraction from the sonicated NB solution shown in Figure 20.

## Discussion

Typical experiments on sonolysis of aqueous solutions of NB have always re-
sulted in oxidation of the aromatic ring as a dominant degradation pathway.
Configuring the sonolysis experiment so that a hard material (metal) is in inti-
mate contact with the horn or the tip of the probe will promote reduction of the
nitro groups of NB rather than oxidation of the aromatic ring. Comparison of
the subsets of by-products from Table 1 and Table 3 shows the differences in the

NB degradation pathway to be quite striking. Metal contact with the tip generates a wider variety of reduction products including dimerization species and products of both reduction and oxidation of the NB such as the aminophenol isomers. Metal contact with the horn rather than the tip seems to initiate only the simple reduction steps of Equation 14, Table 4. Further experiments will ensure that this result is not due to inefficient organic solvent extraction or instrument error.

Since the two different metal wires produced similar reduction behavior, this effect may be due in large part to extreme heating of the metal wires when in contact with the vibrating horn and reflect reducing ability of hot metals. Wires that are not in direct contact with the horn do not vibrate violently enough to heat. Further experimentation with other metal wires will ascertain the effects of the metal composition.

Previous research (Doktycz and Suslick 1990) has shown that cavitation produces shock waves that cause metal particulates to collide with one another so intensely that interparticle melting occurs. Collision intensity depends on particle size; large particles are not accelerated enough to cause melting on impact. The iron oxide (>2 $\mu$m) powder used here may have been small enough to create hot metal but reduction by this hot metal was not observed. The iron and nickel powders may have been too large to cause rapid acceleration, thus reduction by these hot metal powders was not a factor.

A final possibility for the reductive mechanism is the presence of the zero-valent metal. A large body of research notes that zero-valent metal is an excellent reducing agent. (See for example Gillham and O'Hannesin 1994; Matheson and Tratnyek 1994). This is especially true of iron and nickel (Gui, Gillham, and Odziemkowski 1994). Stainless steel is primarily composed of iron; the reduction mechanism observed may be due to degradation of the wire into metallic particulates, followed by oxidation of the zero-valent metal according to the following reaction: $M^0 \rightarrow M^{2+} + 2e^-$.

The electrons are now available to participate in the following reaction:
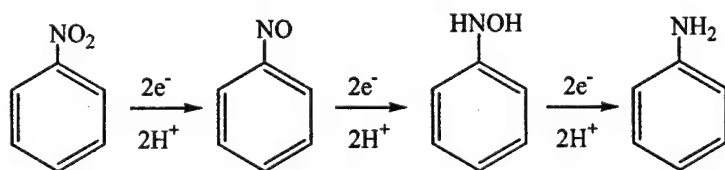


Use of the zero-valent powders, however, should also demonstrate this pathway.

A final point of interest is that neither of the above explanations for enhanced reduction adequately explains why the oxidative mechanism is turned off. It would seem that sonolytic oxidation of NB would still be possible in addition to the reduction process. Table 3 lists only reduced by-products of NB. Phenol and aminophenol likely use aniline as a precursor, indicating that oxidation can occur only on species that have already been reduced.

Lowering the sound amplitude has two effects. First, as expected, the degradation of NB is diminished and few transformation products are formed. Second, while nitrosobenzene is the major product, the presence of phenol and nitrophenol indicates that oxidation is also a viable pathway. Thus, an amplitude effect alone does not eliminate oxidation of NB while maintaining the degradation rate.

This is not the first instance of sonochemical reduction of aromatic nitro groups to aromatic amines. Rusinov et al. (1992) have shown that, with zinc powder and ammonium chloride in ethanol under basic conditions, aromatic nitro groups can be reduced to hydroxylamines. Also, NB can be converted to aniline using iron powder and hydrazine hydrate in ethanol (Pyo and Han 1995). The experiments reported here, however, do not need the addition of catalysts or additional hydrogen donors to cause reduction.

The reduction by-products obtained in this work agree well with expected by-products based on biological and electrochemical reduction of nitroaromatic molecules. 2,4-Dinitrotoluene (DNT) is reductively transformed by microorganisms through the nitroso and hydroxylamine analogues to diaminotoluene (McCormick, Cornell, and Kaplan 1978). Several dimers were also formed from combinations of these analogues to the dinitroazoxytoluene compounds. Similar products were also observed due to electrochemical reduction of DNT at a graphite carbon cathode (Meenakshisundaram et al. 1999).

As noted previously (Meenakshisundaram et al. 1999), the nitro group generally protects the compound from biological attack. Development of a degradation method that specifically focuses on transformation of the nitro group can serve as an initial treatment step for subsequent biological degradation. In addition, the reduction of nitro groups has been described as synthetically important and this method may be useful as an organic reaction.

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**14. ABSTRACT**

Nitroaromatic compounds with energetic characteristics are frequently present in waste streams produced at U.S. Army facilities. Previous work on the sonolytic destruction of nitroaromatic species in aqueous solutions involved primarily denitration together with oxidation via hydroxyl radical attack.

Subjecting a chemical reaction to ultrasound, with frequencies roughly between 15 kHz and 10 MHz, can have a drastic effect. Ultrasound causes acoustic cavitation — the creation, growth, and collapse of bubbles in the solution. The collapse produces localized spots of extreme conditions including temperatures as high as 5000 K and pressures near 1000 atmospheres. The extreme conditions thus created initiate three distinct destruction pathways for organic contaminants: oxidation by hydroxyl radicals, supercritical water oxidation, and pyrolysis. These three mechanisms account for the degradation mechanisms for organic species in water. Interest in ultrasound for decontamination arises from its ability to cause these effects relatively inexpensively, with simple equipment and without severe experimental conditions.

In this report, a simple mechanical manipulation of the experimental apparatus is shown to greatly alter the degradation pathway to promote reduction of the nitro group rather than oxidation of the aromatic ring. This work describes this experimental change and demonstrates the sonochemical reduction of nitrobenzene.

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